Supporting Information for:

Toxic Byproduct Formation during Electrochemical Treatment of Latrine Wastewater

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18 pages
9 figures
4 tables

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Analytical Methods. HAAs and THMs were quantified by GC/MS (HP 6890 GC/HP 5973 MS). Disinfection by-products were separated by a Phenomenex Zebron ZB-WAX column (30 m x 0.25 mm x 0.25 μm df) using He at 1 mL min^{-1} (6 psi). The injector was held at 200 °C and a sample volume of 3 μL (splitless) was used. For THMs, the oven was set at 30 °C (hold for 2 min) and then ramped as follows: 5 °C min^{-1} to 50 °C (hold 2 min); 35 °C min^{-1} to 150 °C (hold 5 min); 25 °C min^{-1} to 185 °C (hold 5 min). For HAAs, the oven was set at 35 °C (hold for 10 min) and then ramped as follows: 5 °C min^{-1} to 75 °C (hold 15 min); 40 °C min^{-1} to 185 °C (hold 5 min). Disinfection by-products were measured in single ion monitoring (SIM) mode at the following mass to charge ratios and dwell times: chloroform (83; 100 ms); bromodichloromethane (83; 100 ms); dibromochloromethane (129; 100 ms); bromoform (173; 100 ms); monochloroacetic acid (MCAA; 59; 250 ms), dichloroacetic acid (DCAA; 59; 250 ms), and trichloroacetic acid (TCAA; 59; 250 ms).

Average Number of Treatment Cycles before Discharge Calculation. In off-the-grid electrochemical wastewater treatment systems, treated wastewater can be used as flushing water to reduce or eliminate water requirements. This design will result in parcels of water being treated multiple times after flushing, potentially increasing electrochemical byproduct concentrations prior to discharge. The average number of treatment cycles a parcel of water will go through prior to discharge can be calculated according to:

$$\text{cycles} = \frac{V_{\text{treated}}}{V_{\text{input}}} = \frac{V_{\text{input}} + V_{\text{flush}}}{V_{\text{input}}} \approx \frac{0.3\ \text{L} + 3\ \text{L}}{0.3\ \text{L}} = 11 \quad \text{(S1)}$$

where $V_{treated}$ is the volume of water to be treated per use, which is the input volume of urine per use (V_{input}) plus the volume of treated water used for flushing (V_{flush}). Typical values of 0.3 L of urine per user and 3 L of treated water per flush were assumed.

Table SI 1. Health guidelines for electrochemically produced by-products in drinking water measured in this study.

Contaminant	US EPA (μM)	WHO (μM)
Chlorate	2.5[(1) a]	8.4[(2) b]
Perchlorate	0.15[(3) c]	0.7[(4) d]
Nitrate	700[(5) e]	3500[(6) f]
Bromate	0.08[(5) e]	0.08[(7) b]
Contaminant	**US EPA (mg L^{-1})**	**WHO (μM)**
THMs [g]	0.08[(8) e]	no guideline
Chloroform	no guideline	3[(9) f]
Bromodichloromethane	no guideline	0.4[(9) f]
Dibromochloromethane	no guideline	0.5[(9) f]
Bromoform	no guideline	0.4[(9) f]
HAAs [h]	0.06[(8) e]	no guideline
MCAA	no guideline	0.2[(10) f]
DCAA	no guideline	0.4[(11) d]
TCAA	no guideline	1[(12) f]

[a] Health reference level. [b] Provisional guideline. [c] Health advisory. [d] Draft guideline. [e] Maximum contaminant level. [f] Guideline. [g] Sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. [h] Sum of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

Table SI 2. Summary of Electrochemical Byproduct Formation in Previous Studies.

Water Treated	Anode	Current Density (mA cm^{-2})	Membrane	$[COD]_{init}$ (mg L^{-1})	$[Cl^-]_{init}$ (mM)	$[NH_4^+]_{init}$ (mM)	[THM] (mg L^{-1})	[HAA] (mg L^{-1})	AOCl (µM)	$[ClO_3^-]$ (mM)	$[ClO_4^-]$ (mM)	$[NO_3^-]$ (mM)	Ref.
RO [a]	BDD [b]	12.5	cation exchange	140	40	0.4	1.3 (1.3)[c]	3.8 (3.8)[c]	800 (250)[c]	-- [d]	--	--	13
RO	BDD	12.5	cation exchange	150	4	--	1.1	8.8	--	--	--	--	14
RO	BDD	12.5	cation exch., none	140	40	--	--	--	560 (200)[c]	--	--	--	15
RO	BDD	2-20	none	130	20	8	0.2 (0.1)[c,e]	--	--	3.6 (1.8)[c,e]	--	2 (2)[c,e]	16
RO	BDD	17	none	160	20	3	--	--	--	4 (4)[c]	--	--	17
RO	BDD	10-30	none	180	20	3	--	--	--	4.2 (4.2)[c]	--	--	18
RO	RuO_2 [f]	10-30	none	180	20	3	--	--	--	0.9	--	--	18
RO	Ir, SnO_2 [g]	12.5	cation exchange	150	4	--	0.7	3.9	--	--	--	--	14
RO	$RuIrO_2$ [h]	10	cation exchange	170	30	0.6	0.3 (0.1)[e]	2.8 (0.8)[e]	--	0.8 (0.2)[e]	0	--	19
Domestic [i]	BDD	10, 20	cation exchange	--	10	--	--	--	20 (8)[c]	1.5 (0.1)[c]	1 (0.4)[c]	--	20
Domestic	BDD	2.5-120	none	--	3	--	--	--	30 (0.4)[j]	0	0	--	21
Landfill [k]	BDD	120-260	none	3400	70	90	2.1	--	--	--	--	4	22
Landfill	PbO_2 [l]	3.0	cation exchange	2800	130	2	--	--	560	--	--	--	23
Latrine [m]	TiO_2 [n]	1.25	none	--	20	5	0.4	0.7	--	--	--	--	24
Latrine	SbSn [o]	25	none	250	30-60	10	--	--	--	10 (3)[c,e]	6 (6)[c,e]	5 (1)[c,e]	25
OO leach. [p]	BDD	0.1, 0.3	none	1000	0.1	20	3.5 (2)[c]	--	--	--	--	--	26
Drinking [q]	BDD	10-30	none	--	1	--	--	--	--	--	1	--	27
Surface [r]	IrO_2 [s]	0-8	none	10	3	--	0.05 (0.03)[j]	0.1 (0.04)[j]	--	0	0	--	28
GW [t]	$RuIrO_2$	11	none	30	2	--	--	--	70	--	--	--	29
Urine	BDD	10-20	none	1710	35	133	3 (2)[c,u]	--	280	20 (20)[c]	30 (10)[c]	--	30
Urine	TDIROF [v]	10-20	none	1710	35	133	1.3 [u]	--	370	28	28	--	30

[a] Reverse osmosis retentate. [b] Boron-doped diamond. [c] Max conc. (conc. upon COD removal). [d] Not measured. [e] Max conc. (conc. upon NH_4^+ removal). [f] RuO_2/Ti. [g] Pt-IrO_2/Ti or SnO_2-Sb/Ti. [h] $RuIrO_2$/Ti. [i] Domestic wastewater. [j] Max conc. (conc. upon disinfection). [k] Landfill leachate. [l] PbO_2/Ti. [m] Latrine wastewater. [n] TiO_2/IrO_2/Ti. [o] Sb-SnO_2/Co-TiO_2/IrO_2/Ti. [p] Olive oil leachate. [q] Drinking water. [r] Surface water. [s] IrO_2/Ti. [t] Groundwater. [u] Only chloroform was measured. [v] Thermally decomposed iridium oxide film.

Table SI 3. Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and Total Inorganic Carbon (TIC) Concentrations during Electrolysis.

Conditions	COD (mg O_2 L^{-1})	TOC (mg C L^{-1})	TIC (mM)
TiO_2/IrO_2 [a] 2.5 A L^{-1} 30 mM Cl^-	0 h: 510 6 h: 440 12.5 h: 370	0 h: 142 12.5 h: 112	0 h: 50 12.5 h: 6
TiO_2/IrO_2 [a] 5.0 A L^{-1} 30 mM Cl^-	0 h: 510 3 h: 400 9 h: 360	0 h: 142 9 h: 82	0 h: 50 9 h: 3
TiO_2/IrO_2 [a] 7.5 A L^{-1} 30 mM Cl^-	0 h: 610 6 h: 296	0 h: 142 6 h: 86	0 h: 51 6 h: 2
TiO_2/IrO_2 [b] 7.5 A L^{-1} 65 mM Cl^-	0 h: 610 6 h: 164	0 h: 152 6 h: 83	0 h: 51 6 h: 4
TiO_2/IrO_2 [b] 7.5 A L^{-1} 100 mM Cl^-	0 h: 432 4 h: 184 12 h: <LOD [c]	0 h: 178 4 h: 128 12 h: 122	0 h: 52 4 h: 4 12 h: 4
BDD [d] 4 A L^{-1} 30 mM Cl^-	0 h: 437 1 h: 120 2 h: <LOD [c] 4 h: <LOD [c] 6 h: <LOD [c]	0 h: 149 6 h: 12	0 h: 55 6 h: 1
NaOCl addition [e]	0 h: 510 2 h: 410 4 h: 270 6 h: 110	0 h: 147 6 h: 117	0 h: 54 6 h: 19

[a] See Figure 2 of main manuscript and Figure SI 4 for concentrations of other species. [c] See Figure 3 of main manuscript and Figure SI 5 for concentrations of other species. [c] Limit of detection (LOD) was 30 ppm O_2. [d] See Figure 4 of main manuscript for concentrations of other species. [e] See Figure 6 of main manuscript for concentrations of other species.

Table SI 4. Measured HAA Electrolysis Rates on BDD Anodes. [a]

HAA	k_{borate} [b] (Ah L^{-1})	$k_{latrine}$ [c] (Ah L^{-1})	k_{borate} [b] (s^{-1})	$k_{latrine}$ [c] (s^{-1})
MCAA	$12.7 \pm 0.4 \times 10^{-2}$	$26 \pm 1 \times 10^{-2}$	$1.9 \pm 0.1 \times 10^{-4}$	$2.0 \pm 0.2 \times 10^{-4}$
DCAA	$8.2 \pm 1.0 \times 10^{-2}$	$25 \pm 1 \times 10^{-2}$	$2.2 \pm 0.1 \times 10^{-4}$	$1.3 \pm 0.1 \times 10^{-4}$
TCAA	$8.4 \pm 2.5 \times 10^{-2}$	$35 \pm 1 \times 10^{-2}$	$2.2 \pm 0.1 \times 10^{-4}$	$1.4 \pm 0.3 \times 10^{-4}$

[a] HAA concentrations are shown in Figure 5 of main manuscript. [b] Borate buffer solution. [c] Latrine wastewater.

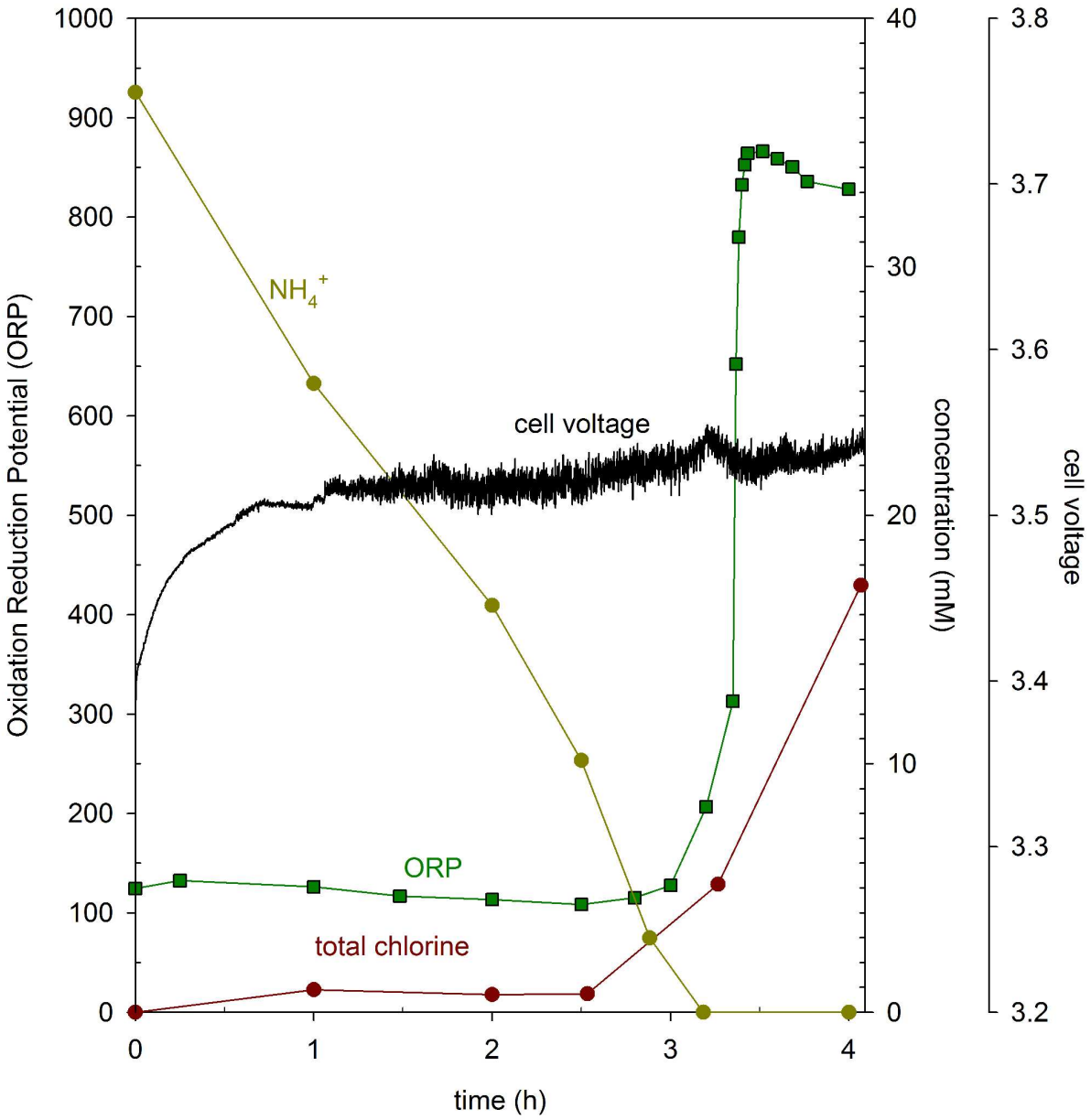

Figure SI 1. Oxidation reduction potential (ORP), total chlorine concentration, cell voltage, and ammonium concentration during electrolysis of latrine wastewater amended with sodium chloride (TiO_2/IrO_2 anodes; 7.5 A L^{-1}; $[Cl^-]_{initial}$=100 mM). Near the breakpoint (complete ammonium removal; ~3.2 h), total chlorine concentrations and ORP spiked. At the same point, cell voltage showed a distinct peak. Lines added for clarity.

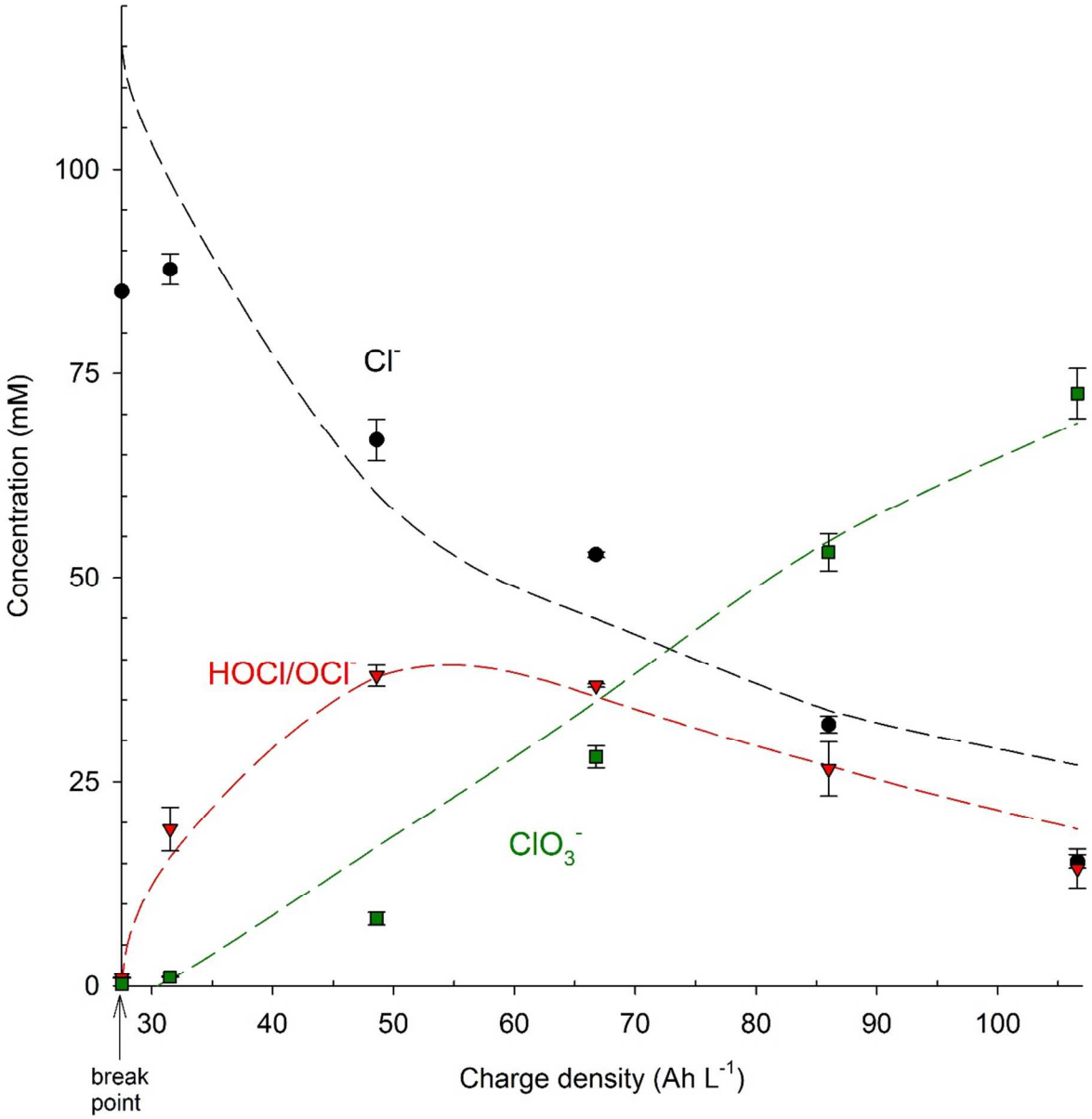

Figure SI 2. Concentrations of measured (symbols) and modeled (dashed lines) chlorine species following the breakpoint during electrolysis of latrine wastewater on TiO_2/IrO_2 anodes at 7.5 A L^{-1}. Reaction rate constants were obtained by fitting reactions ($2Cl^- + H_2O \xrightarrow{k_1} OCl^- + Cl^- + 2H^+ + 2e^-$; $OCl^- + 2H_2O \xrightarrow{k_2} ClO_3^- + 4H^+ + 4\,e^-$)[25] to the experimental data ($k_1 = 0.35\ M^{-1}$ (Ah L^{-1})$^{-1}$; $k_2 = 0.030$ (Ah L^{-1})$^{-1}$). See Figure 1 of main manuscript for concentrations of other species.

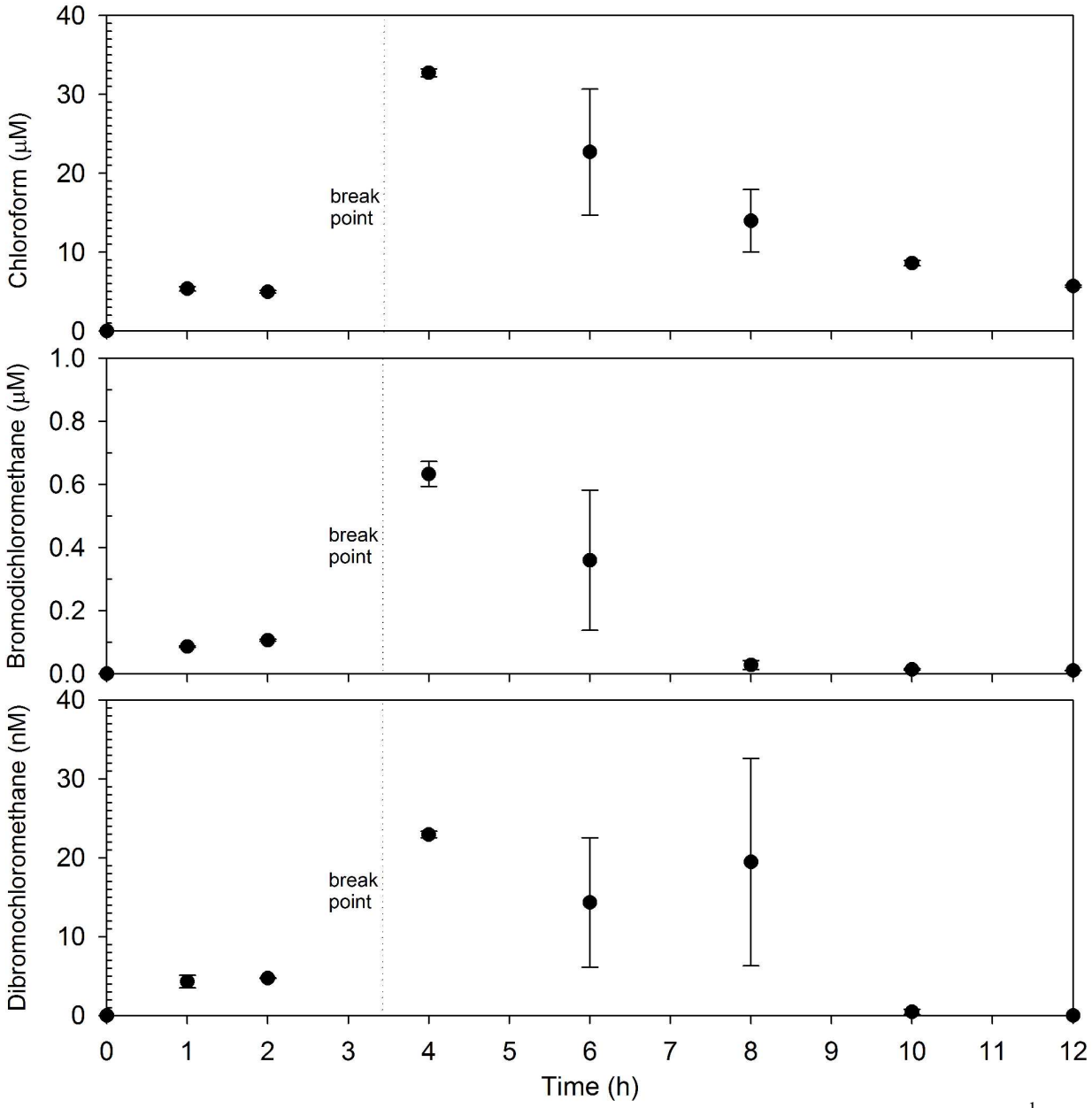

Figure SI 3. Trihalomethane concentrations during electrolysis (TiO_2/IrO_2 anodes; 7.5 A L^{-1}; 3.8 V) of latrine wastewater amended with sodium chloride ($[Cl^-]$=100 mM). Bromoform was not detected. Dotted lines indicate where the chlorination breakpoint was reached (i.e., complete ammonium removal).

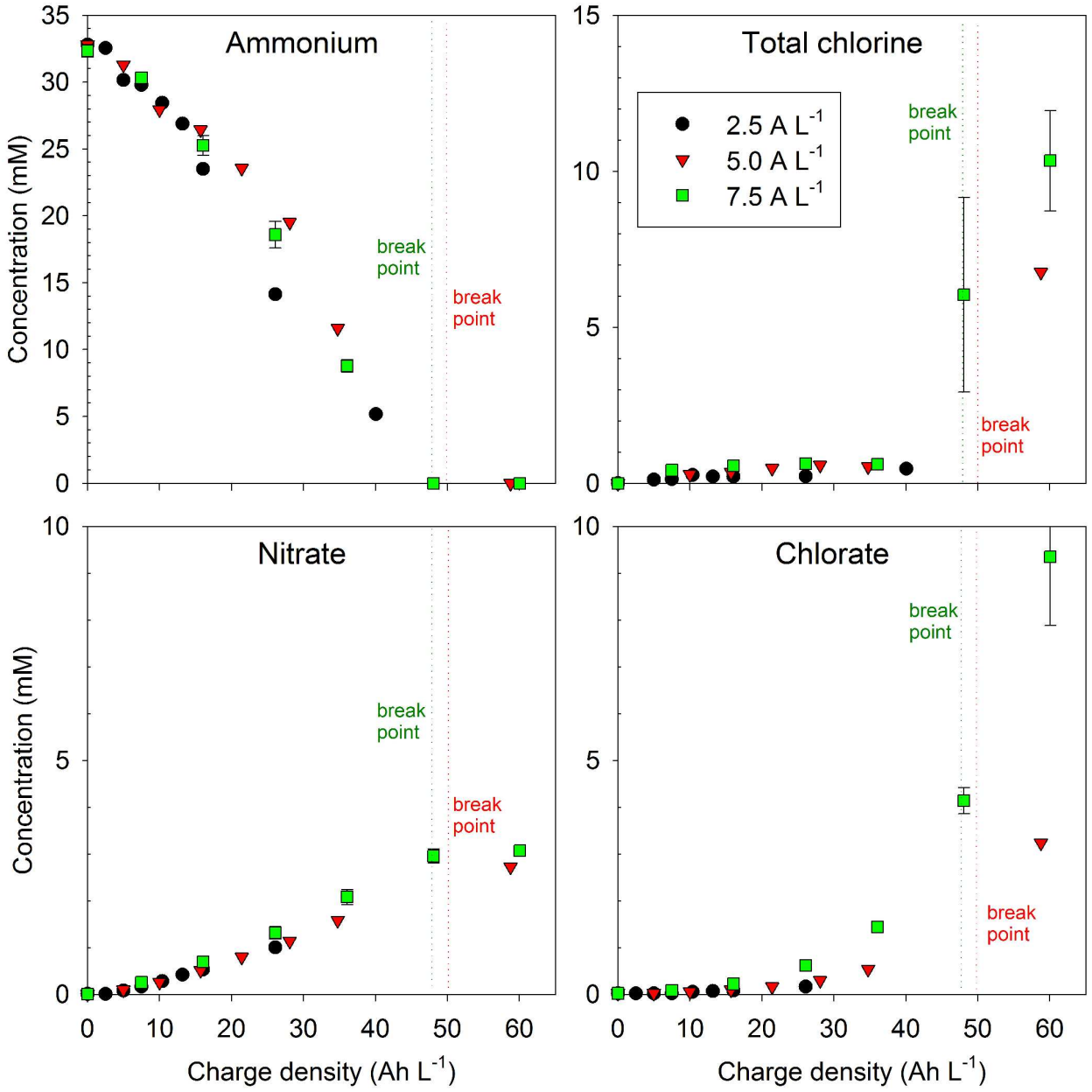

Figure SI 4. Ion and inorganic byproduct concentrations during electrolysis of latrine wastewater at various current densities with TiO_2/IrO_2 anodes. Average cell voltages: 2.5 A L^{-1}: 3.6 V; 5.0 A L^{-1}: 4.0 V; 7.5 A L^{-1}: 4.4 V. Dotted lines indicate where the chlorination breakpoint was reached (i.e., complete ammonium removal).

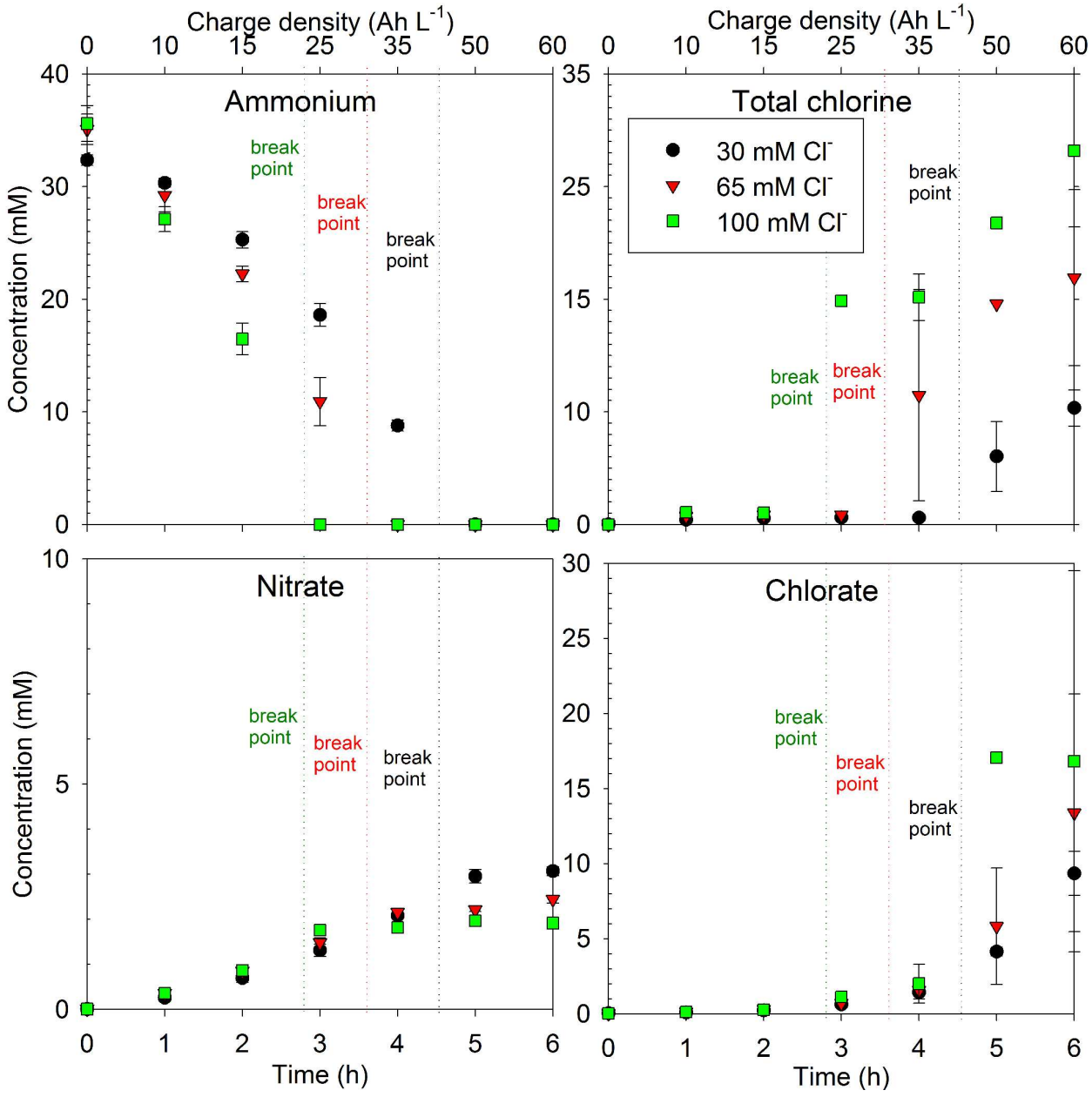

Figure SI 5. Ion and inorganic byproduct concentrations during electrolysis of latrine wastewater at various chloride concentrations with TiO_2/IrO_2 anodes at 7.5 A L^{-1}. Average cell voltages: 30 mM Cl^-: 4.4 V; 65 mM Cl^-: 4.0 V; 100 mM Cl^-: 3.9 V. Dotted lines indicate when the chlorination break point was reached (i.e., complete ammonium removal).

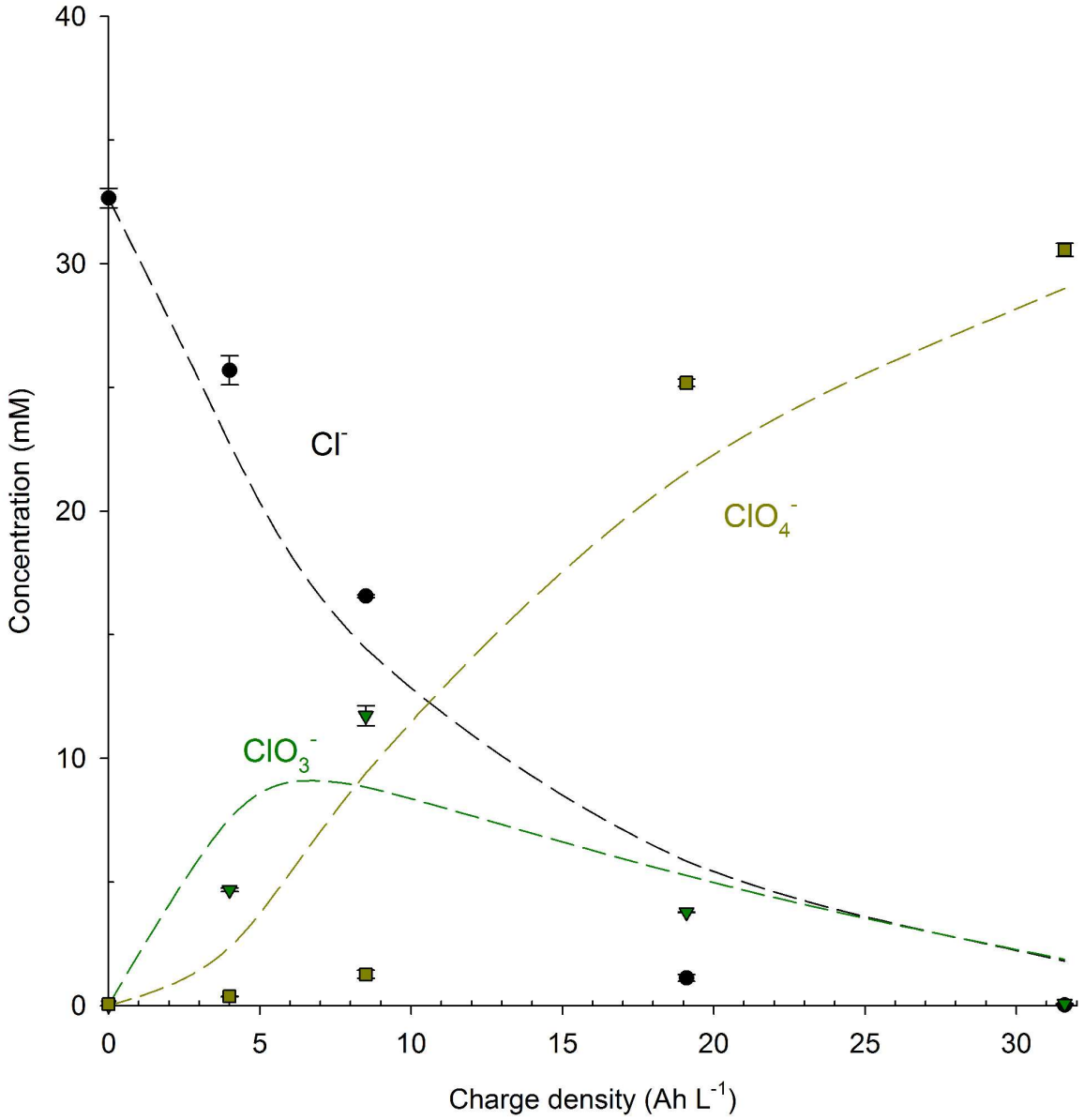

Figure SI 6. Concentrations of measured (symbols) and modeled (dashed lines) chlorine species during electrolysis of latrine wastewater on BDD anodes at 4.0 A L^{-1}. First-order reaction rate constants were obtained by fitting the model ($Cl^- + 3H_2O \xrightarrow{k_3} ClO_3^- + 6H^+ + 6e^-$; $ClO_3^- + H_2O \xrightarrow{k_4} ClO_4^- + 2H^+ + 2e^-$) to the experimental data (k_3 = 0.17 (Ah L^{-1})$^{-1}$; k_4 = 0.087 (Ah L^{-1})$^{-1}$). See Figure 4 of main manuscript for concentrations of other species.

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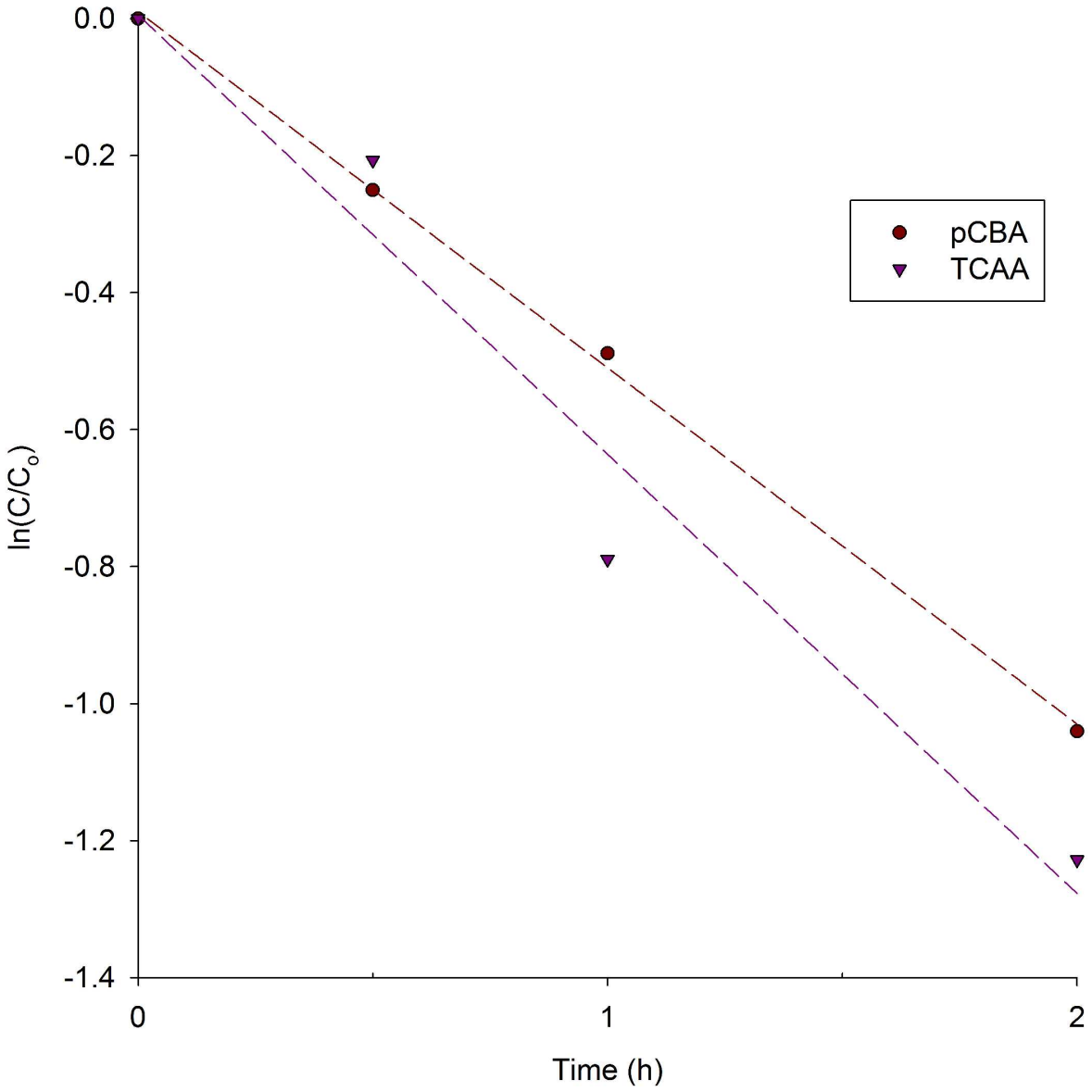

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127 Figure SI 7. Natural log of normalized TCAA and pCBA concentrations during electrolysis in
128 borate buffer on BDD anodes (30 mM; pH 8.7).

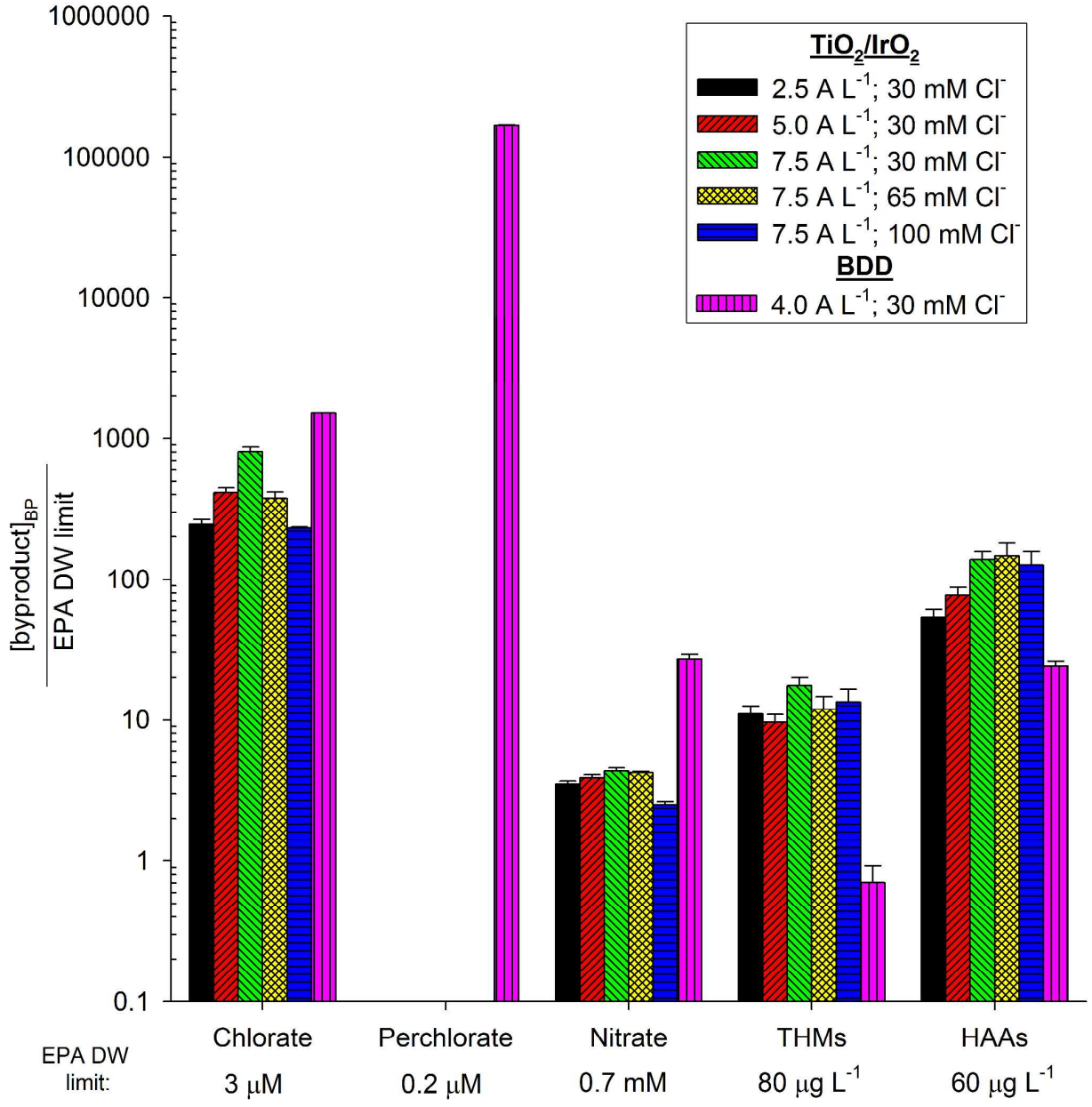

Figure SI 8. Factors that byproduct concentrations near the chlorination breakpoint ([byproduct]$_{BP}$) exceeded US Environmental Protection Agency (EPA) drinking water (DW) advisories and limits after one treatment cycle with different anodes, current densities, and chloride concentrations. For treatment with BDD anodes, the point that chloride was removed was used instead of the breakpoint, because complete ammonium removal was not achieved.

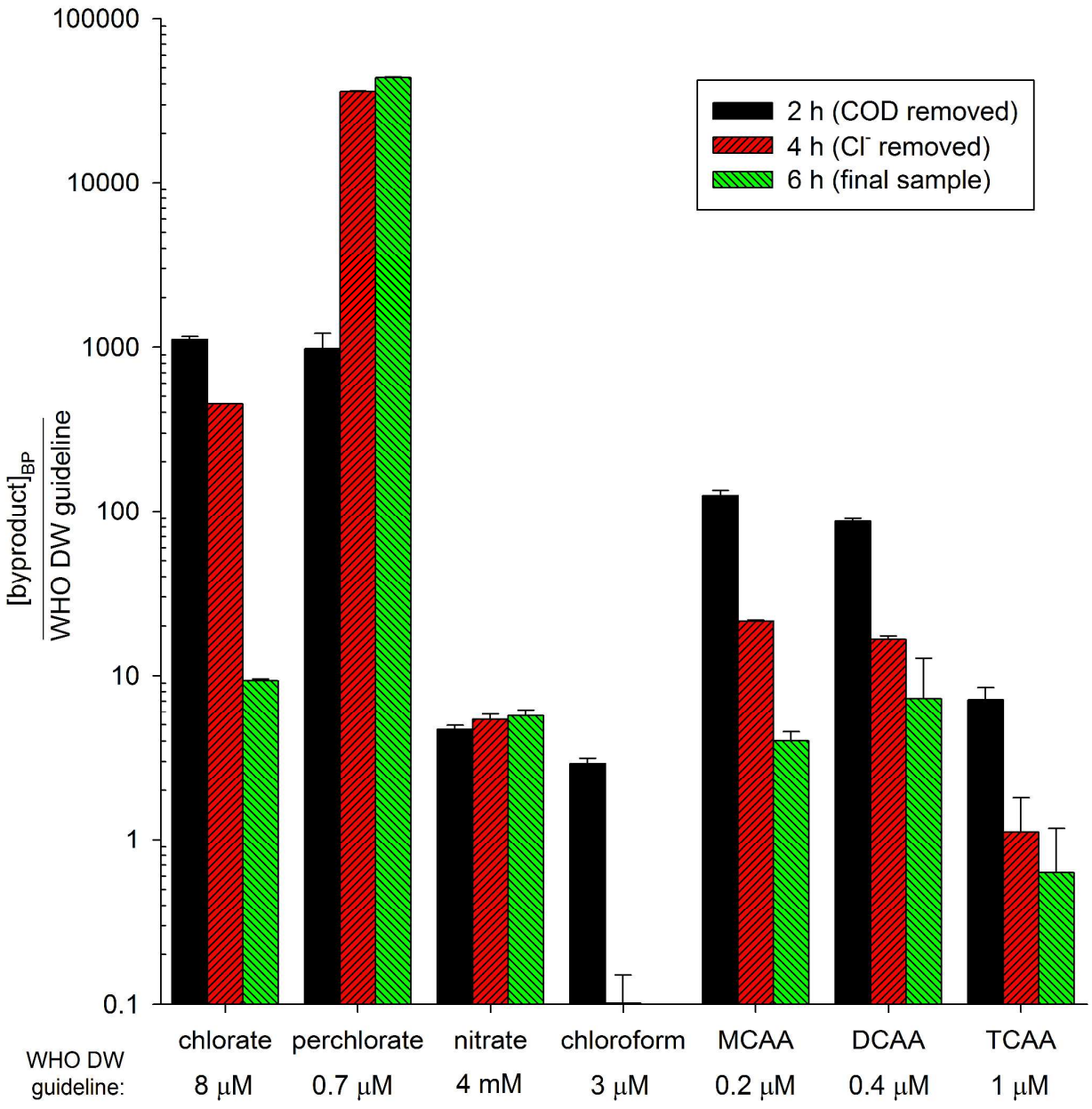

Figure SI 9. Factors that byproduct concentrations near the chlorination breakpoint ([byproduct]$_{BP}$) exceeded World Health Organization (WHO) drinking water (DW) regulations throughout one treatment cycle of latrine water electrolysis with BDD anodes. 4.0 A L^{-1}; 30 mM Cl^- initially.

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